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RADIUM 226 IN WATER (TOTAL, SUSPENDED, AND DISSOLVED) BY RADON DE-EMANATION

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RADIUM^{226} IN WATER (TOTAL, SUSPENDED, AND DISSOLVED) BY RADON DE-EMANATION

by

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16. Abstracts Emanation indicates the general method of approach to determine Radium 226. Ra 226 decays to form Radon 222, a gas separated by aeration and measured for counting alpha disintegrations in gases. A sample is obtained in solution and radium isotopes are coprecipitated with a large amount of barium sulfate. Barium-radium sulfate is decomposed by forming with phosphoric acid, and the resulting glassy melt is dissolved by evaporation with dilute hydrochloric acid to form soluble barium-radium phosphates and chlorides. After aging, radon is removed by aeration and counted. The amount of Ra 226 is calculated from the observed counting rate and the period of ingrowth for Radon 222.

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1. GENERAL DISCUSSION

1.1. Principle: The term "emanation method" does not uniquely define a procedure for the determination of Radium^{226}, but, rather, indicates the general approach to the determination. Ra^{226} decays to form Radon^{222}, a gas, which is separated by aeration and measured by suitable methods for counting alpha disintegrations in gases. Such methods are sensitive, accurate, precise, and extremely versatile when preceded by good chemical practices.

In the methods which follow, the sample is obtained in solution, the radium isotopes are coprecipitated with a rather large amount of barium sulfate, the barium-radium sulfate is decomposed by fuming with phosphoric acid, and the resulting glassy melt is dissolved by evaporation with dilute hydrochloric acid to form soluble barium-radium phosphates and chlorides. The latter are dissolved and transferred to a bubbler. After ageing for a suitable period (a few days to a few weeks), the radon is removed by aeration and counted by a scintillation counting technique. The amount of Ra^{226} in the bubbler and sample is calculated from the observed counting rate and the period of ingrowth for the Rn^{222}.

1.2. Concentration techniques: Barium compounds are excellent carriers for radium because of the similar chemical properties of the two elements. In the described method, one hundred mg of barium is used as the carrier and is precipitated by sulfuric acid. The proportion of barium and radium remaining unprecipitated is negligible and is not detectable except with samples containing large amounts of Ra^{226}. In emanation methods, the amount of barium carrier is limited only by the solubility of the barium chloride in the final solution and by the

radium impurity which is always present in barium salts.

1.3. Interferences: Since the Rn^{222} is removed from the solution by aeration, only gaseous alpha-emitting radionuclides interfere, namely, Rn^{219} (actinon) and Rn^{220} (thoron). Their half-lives are 3.92 seconds and 54.5 seconds, respectively; hence, at the time of the final de-emanation, their presence would indicate the presence of their parents, Ra^{223} and Ra^{224}, respectively. Maximum interference effects from the Ra^{223} and Ra^{224} have been calculated and are very much less than the effects produced by these two radium isotopes when the determination is by non-emanation techniques (19). The short-lived radon isotopes decay before the radon is counted; it is their alpha emitting decay products which actually interfere. These interferences are very rare in water samples, but have been observed in certain uranium mill effluents.

In water, stable chemical interferences are limited because of the relatively few substances which significantly contaminate barium sulfate precipitated from acid solution. Small amounts of lead, calcium, and strontium collected by the barium sulfate do not interfere, but lead may attack the platinum. Calcium at concentrations of 300 mg per liter does not cause difficulty. Total dissolved solids at concentrations of 269,000 mg per liter do not affect the recovery of radium.

The method for dissolved Ra^{226} in water is applicable to uranium mill effluents, if they are evaporated after 4.2 and wet-ashed with nitric and sulfuric acids. After ashing, the sample is diluted to its original volume, digested overnight on a steam bath to convert poly-phosphates to orthophosphate, cooled, and the analysis continued at 4.3. More HF may be needed in 4.5 since effluents often contain a considerable amount of silica.

With suspended solids, a small flocculent precipitate of zirconyl phosphate may be present in the final solution. This does not prevent the removal of the radon when the amount of carrier is that specified.

Small orange-yellow precipitates sometimes appear in the final solution. These are probably chloroplatinates and do not affect the results.

1.4. Minimum detectable concentration: The minimum detectable concentration depends upon the electrical background of the counter, the background counting rate of the scintillation cell, the statistical accuracy of the counting, the radium content of the reagents, and the degree of contamination from apparatus and the environment. Without reagent purification, the over-all blank is about 0.03 to 0.05 $\mu\mu g$ Ra^{226}, and this is about the minimum detectable quantity of Ra^{226}. Therefore, on a one-liter sample, the minimum detectable concentration is about 0.04 $\mu\mu g$ Ra^{226} per liter. With larger samples, long counting times, and purified reagents, the minimum detectable concentration can be reduced further.

2. APPARATUS

2.1. Counting instruments: One of the following arrangements of counting equipment is required:

a. A complete scintillation counter with 2 inch (or larger) photomultiplier tube mounted vertically with its face up in a light-tight housing. The housing must be large enough to contain the scintillation cell described in 2.2; or

b. A scintillation counting accessory equipped with a photomultiplier tube mounted and housed as specified in 2.1 a. and a compatible proportional counter (or scaler).

2.2. Scintillation cell, Lucas type, having volume of 95-140 ml. Made in laboratory (17, 19) or obtained commercially*(Figure 1).

2.3. Membrane filtering assembly and filters, including vacuum source.

2.4. Radon bubblers, one for standard radium solution and one for each sample, according to reference (19). Total volume, fritted glass disc to stopper, 18 to 25 ml. Available from Corning Glass Works, Special Apparatus Division (Figure 2).

2.5. Manometer, open-end, capillary (1-1/2 mm I.D.), mounted on meter stick and ring stand (Figure 3).

2.6. Gas purification tube, 7 to 8 mm O.D. glass tubing, 100-120 mm long, constricted at lower end to hold glass wool plug (Figure 3).

2.7. Plastic bottles, polyethylene, with polyethylene or plastic-lined caps, 1/2 to 1 gallon capacity.

2.8. Compressed air, cylinder, with two-stage pressure regulator, aged 30 days to allow decay of radon.

2.9. Paraffin

2.10. Sealing wax, "Pyseal", low-melting

2.11. Silicone grease, high-vacuum

2.12. Glassware: Volumetric flasks (100 ml, 1000 ml), pipettes (10 ml, 100 ml), graduates (5 ml, 25 ml, 50 ml, 1000 ml), burette (50 ml), stirring rods (assorted), beakers (250 ml, 400 ml, 600 ml, 1500 ml), cover glasses (assorted), medicine droppers (marked at 1 ml), and wash bottles.

All glassware, unless new, must be decontaminated as follows: Heat for one hour in 1 per cent EDTA- 1 per cent Na_2CO_3 solution at 90-100°C, rinse with water, rinse with 1:9 HCl, and finally rinse with distilled water. This treatment dissolves barium-radium sulfate.

2.13. Platinum ware: Crucibles (20 to 30 ml) or dishes (50 to 75 ml), platinum-tipped tongs (preferably Blair type), and large dish (for flux preparation).

Clean platinum ware by immersing and rotating it in a molten bath of potassium pyrosulfate, cooling, rinsing in hot tap water, digesting in hot 1:1 HCl, rinsing in distilled water, and igniting over a burner.

2.14. Analytical balance

* Scintillation cells are available from William H. Johnston Laboratories, Inc., 3617 Woodland Avenue, Baltimore 15, Maryland.

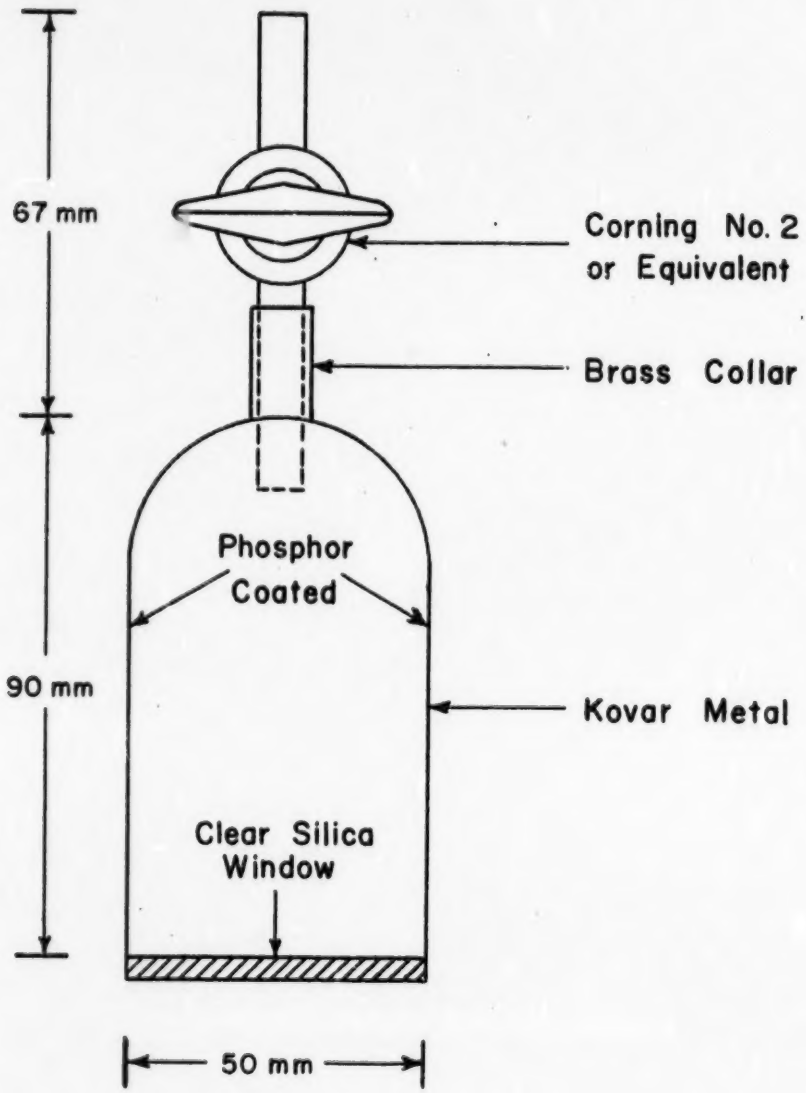

Figure 1. Scintillation Cell

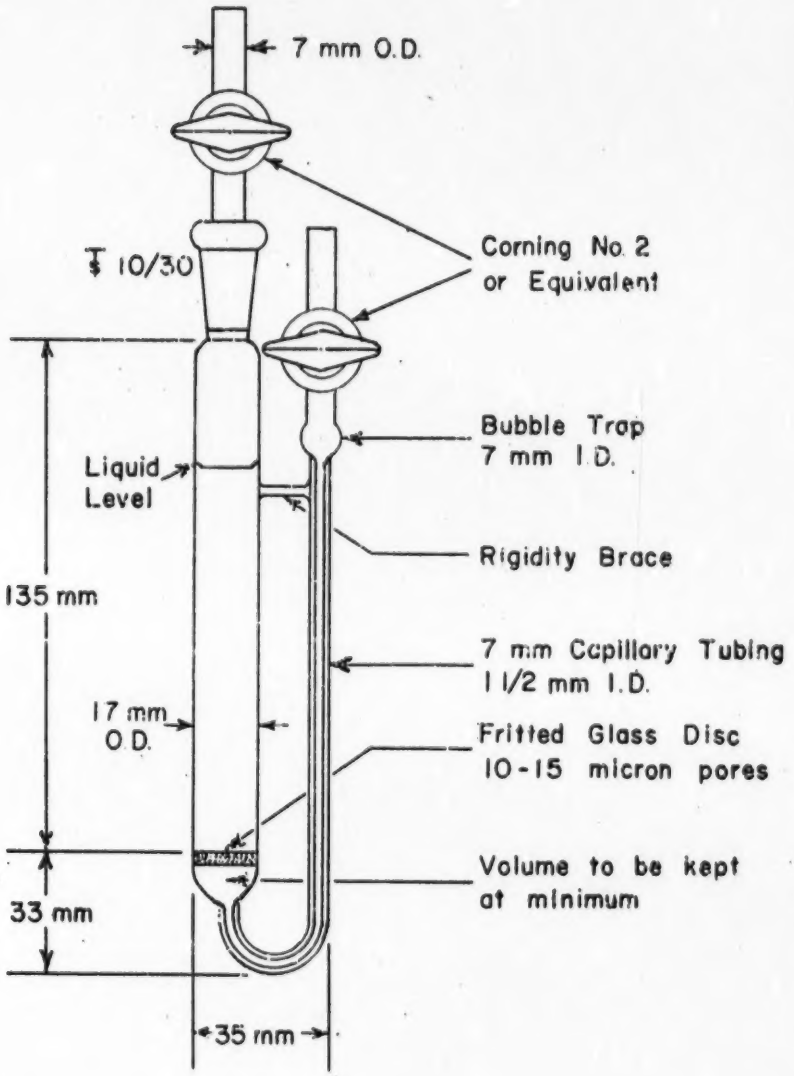

Figure 2. Radon Bubbler

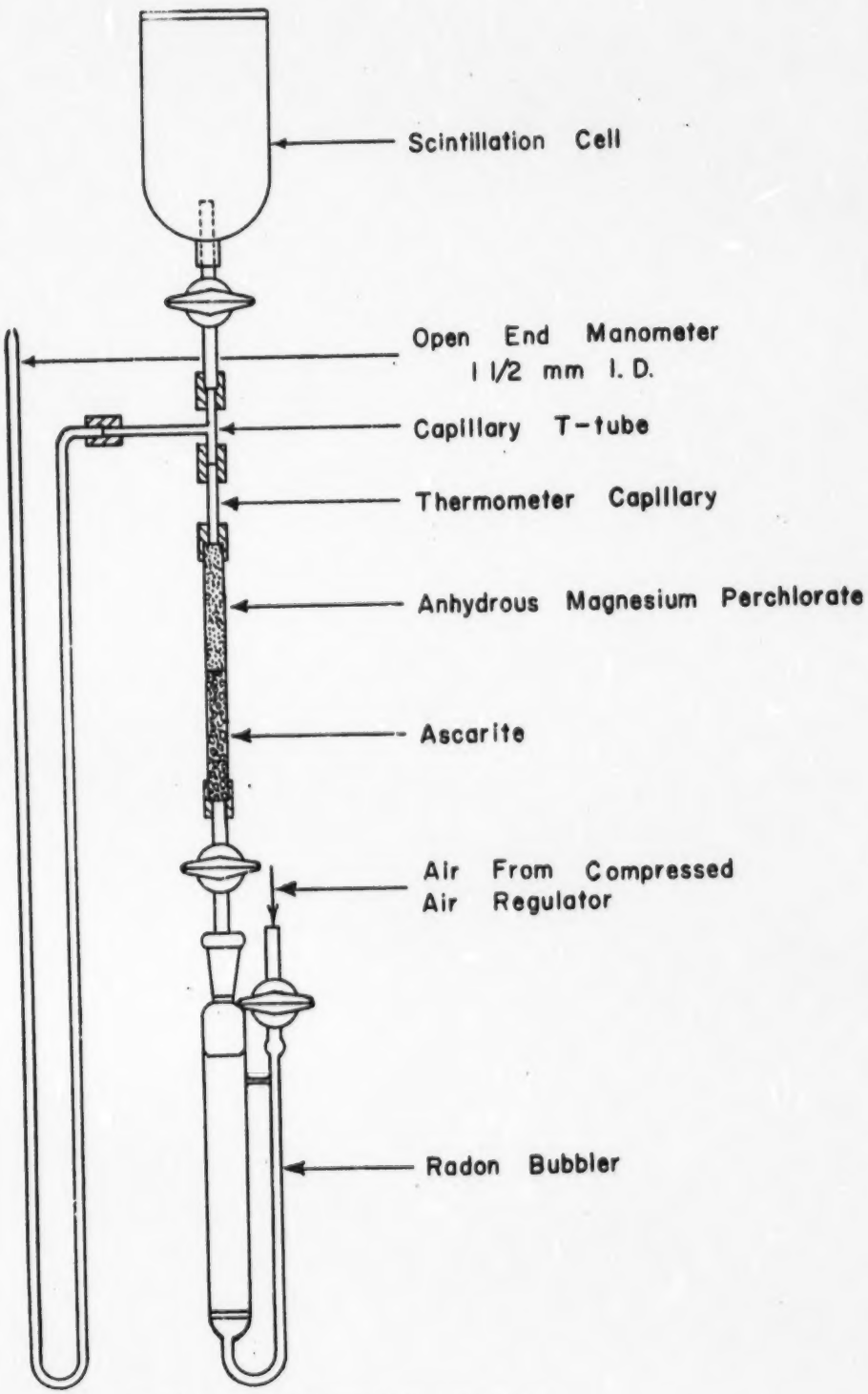

Figure 3. De-emanation Assembly

3. REAGENTS

3.1. Ammonium sulfate solution: Dissolve 10 g $(NH_4)_2SO_4$ in water and dilute to 100 ml in a graduate.

3.2. Ascarite, 8-20 mesh.

3.3. Barium chloride carrier solutions:

a. Stock solution: Dissolve 35.6 g $BaCl_2 \cdot 2H_2O$ in water and dilute to 1 liter. Store in polyethylene bottle for prolonged periods.

b. Working solution: Dilute 100 ml of the stock solution to 1000 ml as needed; 1 ml contains 2 mg Ba^{++}.

3.4. Ethylenediaminetetraacetic acid tetrasodium salt-sodium carbonate decontaminating solution: Prepare a large volume of this solution, using 10 g of each reagent per liter. Store after each use.

3.5. Hydrochloric acid, conc., 1:3, 1:100, and 2N

3.6. Hydrofluoric acid, 48 per cent (in dropping-type bottle).

3.7. Magnesium perchlorate, anhydrous (desiccant).

3.8. Phosphoric acid, conc. (85 per cent).

3.9. Diluting solution for radium standard: Dilute 100 ml stock barium chloride solution (20 mg Ba^{++} per ml (3.3)) to 1980 ml. Let stand overnight, filter through membrane filter, add 20 ml conc. hydrochloric acid, and mix.

3.10. Standard Ra^{226} solution and Standard Bubbler: Use National Bureau of Standards radium gamma-ray standard. (The lowest available standard contains 0.1 μg Ra^{226}; the use of this standard is desirable since it requires less dilution and does not present as severe a contamination problem as do the higher standards. Because of the very high activity of the standard extreme precautions are necessary in handling

the standard to avoid contaminating the equipment and the work area.) Place the ampoule in a 600 ml beaker and cover it with about 300 ml of diluting solution (3.9). Break ampoule neck with a stout rod; chip ampoule until it is broken or until the hole is large enough to make mixing and rinsing effective. Mix and transfer solution to a 1-liter volumetric flask. Dilute to mark and mix. Continue dilutions with diluting solution in ten-fold steps until a Ra^{226} conc. of 10 $\mu\mu$g Ra^{226} per ml is reached. Add 30.00 ml of the last solution (10 $\mu\mu$g Ra^{226} per ml) to a 100-ml volumetric flask, dilute to the mark, and mix. One ml contains approximately 3 $\mu\mu$g Ra^{226}. Correct for decay of Ra^{226} since its standardization by NBS. To a radon bubbler add 1 ml strong barium chloride carrier (20 mg Ba^{++} per ml), 10.00 ml of the final standard Ra^{226} (approximately 3 $\mu\mu$g Ra^{226} per ml), and enough diluting solution to fill bubbler about three-fourths full. Seal and close bubbler and mix contents as directed in 4.14.

3.11. Flux, (not needed in dissolved radium determination): To a large platinum dish (about 500 ml capacity) add 30 mg $BaSO_4$, 65.8 g K_2CO_3, 50.5 g Na_2CO_3, and 33.7 g $Na_2B_4O_7 \cdot 10\ H_2O$. Mix well and heat cautiously until the water is expelled; fuse and mix thoroughly by swirling. Cool flux, grind it in a porcelain mortar to pass a 10-mesh (or finer) screen. Store in an air-tight bottle. (Flux can be prepared in smaller batches in smaller dishes.)

3.12. Sulfuric acid, conc., 1:200

3.13. Hydrogen peroxide, 3 per cent: Dilute 30 per cent H_2O_2 in ratio of 1 volume 30 per cent H_2O_2 to 9 volumes of water.

4. PROCEDURE FOR DISSOLVED RADIUM^{226} IN WATER

Water samples are filtered through membrane filters as soon after collection as is possible. (Filters may be saved for analysis by Section 5, if desired.) They are acidified immediately with 2 per cent by volume of concentrated hydrochloric acid and stored in polyethylene bottles prior to analysis. In the case of uranium mill effluents, the sample for analysis is to be taken immediately after filtration to prevent precipitation during storage.

4.1. To 1020 ml of the acidified water sample in a 1500-ml beaker, add with vigorous stirring 50 ml of dilute $BaCl_2$ carrier solution. A blank consisting of distilled water is similarly treated and started at this step.

4.2. Add slowly and with vigorous stirring 20 ml conc. H_2SO_4. Cover and let stand at room temperature overnight.

4.3. Filter through a membrane filter, transfer precipitate quantitatively to filter with 1:200 H_2SO_4, and wash filter twice with 1:200 H_2SO_4.

4.4. Transfer filter and precipitate to platinum crucible (or small platinum dish); with a fine jet of water, transfer any precipitate which adheres to the filtration apparatus to the platinum vessel.

4.5. Add 0.5 ml (10 drops from dropping bottle) HF, add 3 drops 10 per cent ammonium sulfate, and evaoporate to dryness.

4.6. Cautiously ignite over a Bunsen burner until organic matter is burned off. Cool.

4.7. From a calibrated dropper, add 1 ml conc. H_3PO_4, heat on hot plate at 200°C, gradually raise the temperature to 300-400°C. Maintain

at this temperature for 30 minutes.

4.8. Hold the platinum vessel (with platinum-tipped tongs) over a low flame and adjust rate of heating to avoid spattering. Swirl the vessel so that the walls are covered with the hot H_3PO_4. Continue heating until the $BaSO_4$ dissolves to give a clear melt (just below redness); continue heating one minute more to insure removal of SO_3. Cool platinum vessel.

4.9. Fill the platinum vessel about half full with 1:3 HCl, place it over live steam, finish filling vessel (to within 2 mm of top) with 1:3 HCl.

4.10. Evaporate on steam bath until $BaCl_2$ crystals, H_3PO_4, and a trace of HCl remain, as judged by cessation of vapors.

4.11. To the platinum vessel add 6 ml 2N HCl, swirl, and warm to dissolve.

4.12. Close inlet stopcock on the radon bubbler. Wet disc with a drop of water. Transfer solution to bubbler with a medicine dropper. Rinse dropper and vessel with three approximately 2 ml portions of distilled water. Be sure that H_3PO_4 is rinsed from the waxed ₹ joint of the bubbler stopper. Dry joint with lint-free paper or cloth.

4.13. Gently warm male and female portions of waxed bubbler ₹ joint-stopper. Insert the stopper with a twisting motion to spread the wax uniformly in the ground joint. Allow joint to cool.

4.14. Close both stopcocks on bubbler and invert several times to mix. Open outlet stopcock and force droplet out of stopper by applying external pressure with a rubber bulb. Leave stopcock open.

4.15. Adjust gas regulator valve so that a very slow stream of gas will flow with the needle valve open. Attach hose from valve to inlet

stopcock of bubbler. Open the inlet stopcock and cautiously raise pressure (by adjusting the regulator valve -- not the needle valve) until bubbles pass through the fritted glass disc at a rate which will produce a froth a few mm deep at the surface of the solution. Continue the aeration (de-emanation) for 20 minutes.

4.16. In rapid succession, close inlet stopcock, remove air hose connection, and close outlet stopcock. Record the date and time.

4.17. Store bubbler for radon ingrowth. See Table 1 (19).

4.18. Evacuate a calibrated scintillation cell whose background has been determined when filled with the aged compressed air. Attach it and the bubbler containing the radium from the sample to the de-emanation assembly as shown in Figure 3.

4.19. Adjust the gas regulator valve to give a very slight flow (and pressure) when the needle valve is open. Attach air hose from needle-valve to inlet stopcock of bubbler. Open needle valve.

4.20. Open the stopcock on the scintillation cell and note the manometer reading. After about one minute, again read the manometer. If no leak is indicated, proceed with the next steps.

4.21. Note the time and with extreme care partially open the outlet stopcock of the bubbler. (Considerable bubbling will take place because of the lowered pressure.) When the bubbling subsides, open the stopcock a little more. Repeat the process until the stopcock is completely open and vigorous bubbling has stopped. Close outlet stopcock of bubbler.

4.22. Very gradually partially open the inlet stopcock of the bubbler. During this process, the rate of movement of bubbles in the capillary inlet tube must be controlled to a slow rate to avoid loss of liquid. When bubbling subsides, open stopcock completely.

TABLE 1

A. Decay of Radon (in Minutes, Hours, and Days)
B. Growth of Radon from Radium (in Days)
C. Multiplicative Factor for Correction of Radon Activity for Decay during Counting (in Hours)

(Based on 3.825 days as half-life of radon)

Time	A. $e^{-\lambda t}$			B. $1-e^{-\lambda t}$	C. $\frac{\lambda t}{1-e^{-\lambda t}}$
	Minutes	Hours	Days	Days	Hours
0	1.000,0	1.000,0	1.000,0	0.000,0	1.000,0
1	0.999,9	0.992,5	0.834,3	0.165,7	1.003,7
2	0.999,8	0.985,0	0.696,0	0.304,0	1.007,5
3	0.999,6	0.977,6	0.580,7	0.419,4	1.011,4
4	0.999,5	0.970,3	0.484,4	0.515,6	1.015,2
5	0.999,4	0.963,0	0.404,1	0.595,9	1.019,0
6	0.999,3	0.955,7	0.337,2	0.662,8	1.022,8
7	0.999,1	0.948,5	0.281,3	0.718,7	1.026,7
8	0.999,0	0.941,4	0.234,7	0.765,3	1.030,5
9	0.998,9	0.934,3	0.195,8	0.804,2	1.034,4
10	0.998,7	0.927,3	0.163,3	0.836,7	1.038,2
11	0.998,6	0.920,3	0.136,3	0.863,7	1.042,1
12	0.998,5	0.913,4	0.113,7	0.886,3	1.046,0
13	0.998,4	0.906,5	0.094,8	0.905,2	1.050,0
14	0.998,2	0.899,7	0.079,1	0.920,9	1.053,8
15	0.998,1	0.892,9	0.066,0	0.934,0	1.057,7
16	0.998,0	0.886,2	0.055,1	0.944,9	1.061,6
17	0.997,9	0.879,6	0.045,9	0.954,1	1.065,5
18	0.997,7	0.872,9	0.038,3	0.961,7	1.069,5
19	0.997,6	0.866,4	0.032,0	0.968,0	1.073,4
20	0.997,5	0.859,9	0.026,7	0.973,3	1.077,4
21	0.997,4	0.853,4	0.022,3	0.977,8	1.081,4
22	0.997,2	0.847,0	0.018,6	0.981,4	1.085,4
23	0.997,1	0.840,6	0.015,5	0.984,5	1.089,3
24	0.997,0	0.834,3	0.012,9	0.987,1	1.093,3
25	0.996,9	0.828,0	0.010,8	0.989,2	1.097,3

TABLE 1 (continued)

Time	A. $e^{-\lambda t}$			B. $1-e^{-\lambda t}$	C. $\frac{\lambda t}{1-e^{-\lambda t}}$
	Minutes	Hours	Days	Days	Hours
26	0.996,7	0.821,8	0.009,0	0.991,0	1.101,4
27	0.996,6	0.815,6	0.007,5	0.992,5	1.105,4
28	0.996,5	0.809,5	0.006,3	0.993,7	1.109,4
29	0.996,4	0.803,4	0.005,2	0.994,8	1.113,5
30	0.996,2	0.797,3	0.004,4	0.995,6	1.117,5
31	0.996,1	0.791,3	0.003,6	0.996,4	1.121,6
32	0.996,0	0.785,4	0.003,0	0.997,0	1.125,7
33	0.995,9	0.779,5	0.002,5	0.997,5	1.129,7
34	0.995,7	0.773,6	0.002,1	0.997,9	1.133,8
35	0.995,6	0.767,8	0.001,8	0.998,2	1.137,9
36	0.995,5	0.762,0	0.001,5	0.998,5	1.142,1
37	0.995,4	0.756,3	0.001,2	0.998,8	1.146,2
38	0.995,2	0.750,6	0.001,0	0.999,0	1.150,3
39	0.995,1	0.744,9	0.000,9	0.999,2	1.154,4
40	0.995,0	0.739,3	0.000,7	0.999,3	1.158,6
41	0.994,9	0.733,8	0.000,6	0.999,4	1.162,8
42	0.994,7	0.728,3	0.000,5	0.999,5	1.166,9
43	0.994,6	0.722,8	0.000,4	0.999,6	1.171,1
44	0.994,5	0.717,3	0.000,3	0.999,7	1.175,3
45	0.994,4	0.712,0	0.000,3	0.999,7	1.179,5
46	0.994,2	0.706,6	0.000,2	0.999,8	1.183,7
47	0.994,1	0.701,3	0.000,2	0.999,8	1.187,9
48	0.994,0	0.696,0	0.000,2	0.999,8	1.192,1
49	0.993,9	0.690,8	0.000,1	0.999,9	1.196,4
50	0.993,7	0.685,6	0.000,1	0.999,9	1.200,6
51	0.993,6	0.680,4	0.000,1	0.999,9	1.204,9
52	0.993,5	0.675,3	0.000,1	0.999,9	1.209,1
53	0.993,4	0.670,2	0.000,1	0.999,9	1.213,4
54	0.993,2	0.665,2	0.000,1	0.999,9	1.217,7
55	0.993,1	0.660,2	0.000,1	1.000,0	1.222,0
56	0.993,0	0.655,2	0.000,0	1.000,0	1.226,3
57	0.992,9	0.650,3	0.000,0	1.000,0	1.230,6
58	0.992,7	0.645,4	0,000.0	1.000,0	1.234,9
59	0.992,6	0.640,5	0.000,0	1.000,0	1.239,2
60	0.992,5	0.635,7	0.000,0	1.000,0	1.243,5

4.23. Carefully open outlet stopcock as directed in 4.21. When both stopcocks are fully open and bubbling has subsided, gradually raise pressure by adjusting the pressure regulator. (Control movement of bubbles in capillary inlet tube as in 4.22.) Continue raising the pressure until the manometer indicates atmospheric pressure within the system.

4.24. Note the time. The elapsed time for the de-emanation should be at least 15 minutes.

4.25. Without delay, close the stopcock on the scintillation cell, close the inlet stopcock on the bubbler, close the outlet stopcock on the bubbler, close the needle-valve, and disconnect the compressed air hose. Again, set the bubbler aside for a possible second de-emanation.

4.26. If counter is not in use, place scintillation cell on photomultiplier tube, cover both with light-tight cover, let stand for about 10 minutes, turn on high voltage, and, after radon has been in cell for four hours, start counting.

4.27. If counter is in use, allow radon to age in cell for four hours. During this period store in dark or subdued light. Place in counter, wait 10 minutes, turn on high voltage, and start counting.

4.28. Compare counting rate with that obtained from the standard radium bubbler with the same scintillation cell. The calibration is carried out by de-emanating the standard bubbler with the scintillation cell as directed in steps 4.14 (omit mixing) through 4.27 and is done prior to the analysis of samples. Unless the scintillation cell is damaged physically, the calibration remains essentially unchanged for years. A 16-hour ingrowth of radon in the standard bubbler produces about 5 $\mu\mu$c of radon; this is a suitable amount of radon for the calibration of the cell, if an overnight count is obtained.

4.29. After the sample has been counted, the radon may be pumped out of the cell. To protect the phosphor, it is necessary to evacuate cells and admit air slowly by gradually opening the stopcock (taking about 15 seconds to open stopcock completely). Attach cell to a good vacuum pump with heavy-walled tubing. Evacuate for 5 to 10 minutes. Remove, admit air, and evacuate again for 10 minutes. Repeat if the radon content was high. Decay products of Rn^{222} will remain in cell, but decay with an effective half-life of about 30 minutes. After the latter activity has died out, the cell is ready for another sample or for a background determination. Ordinarily, a cell can be used once a day.

4.30. Unless it is desired to check the analysis by a second deemanation, discard the radium solution from the bubbler which was set aside in 4.25. If the bubbler contained no more than 10 $\mu\mu$g Ra^{226}, a thorough rinsing with dilute HCl (1:100) is a satisfactory cleansing procedure. To do this, proceed as follows: Attach outlet stopcock to a suction flask by means of Tygon tubing; attach Tygon tubing to inlet stopcock; invert bubbler and clamp on a ring stand; dip free end of tubing in 100 ml of 1:100 HCl; turn on vacuum and open outlet stopcock to empty bubbler; open inlet stopcock to rinse fritted glass disc and bubbler; after a few mls have gone through, close outlet stopcock and let rinse solution accumulate in bubbler until it is about three-fourths full; open outlet stopcock; repeat the process until the rinse solution is all used; place bubbler in upright position and let it drain for a few minutes; using the vacuum, draw out most of the solution through the inlet capillary tube.

Gently warm the stopcock until the wax, "Pyseal", melts. Remove the stopper with a twisting motion. Allow stopper and joint

to cool. The bubbler is now ready for another sample.

If Ra^{226} in bubbler was more than 10 μμg, remove most of the solution by rinsing as described above. Disassemble the bubbler, remove most of the stopcock grease and the sealing wax mechanically or by cloth or swabs moistened with solvents (kerosene for grease; benzene for wax), and immerse for one hour in hot (90-100°C) EDTA-sodium carbonate solution. (Preheat bubblers gradually to avoid thermal shock to discs.) Be sure solution is in disc by drawing a few ml through it. Remove, cool, and rinse (with suction) with distilled water. Immerse in 1:9 HCl and warm for about 30 minutes. Remove, cool, and rinse with distilled water. Dry overnight or in oven. Regrease stopcocks and rewax stopper. Avoid excess of grease and wax.

Occasionally, more drastic cleaning methods may be desirable. Hot kerosene or hot 10 per cent alcoholic KOH will remove grease. Hot conc. HNO_3 will remove most organic matter except stopcock grease. Avoid prolonged contact of discs with alkaline solutions, especially alcoholic KOH which is very corrosive. Avoid the use of H_2SO_4 in bubblers.

5. PROCEDURE FOR RADIUM^{226} IN SUSPENDED MATTER

In general, the suspended matter in water contains siliceous matter which is not soluble in acids. Hence, reliance must be placed on a fusion to get the siliceous substances and the radium into solution. The special flux employed makes it possible to precipitate and filter barium-radium sulfate from the acidified solution of the melt without removal of the silica. With other alkaline fluxes, silica precipitates and interferes with the filtration.

For preliminary treatment of water sample see discussion in Section 4. The suspended matter is collected from a measured volume of water by filtration through a membrane filter. As written, the method can accommodate as much as one gram of inorganic suspended matter.

5.1. Place the membrane filter and suspended matter filtered from a measured volume of water in a weighed platinum crucible (20 to 30 ml capacity). Ash filter and organic matter as described in 4.5 (omitting HF addition) and 4.6.

5.2. Weigh crucible plus residue.

5.3. Add flux to the crucible in the ratio of 8 g flux to 1 g of residue, but use at least 2 g of flux. If weight of flux is reduced, reduce volumes of reagents and solutions in 5.7 and 5.10 proportionately. The amounts indicated in these steps are for 8 g of flux.

5.4. Mix flux and sample with a glass rod.

5.5. Heat over a burner until fusion and reaction starts; then, carefully heat at a rate which will prevent spattering. When reaction (bubbling) ceases, continue heating over a Meker burner for about 20 minutes. The crucible must be swirled occasionally (platinum-tipped

tongs) and its contents must be examined to determine whether or not undecomposed sample remains. The fusion must be continued until decomposition is complete. The melt will not become clear except with high silica or very small samples.

5.6. When decomposition of the sample is complete, rotate the crucible as the melt cools so that the liquid spreads and solidifies in a thin layer on the crucible wall. Allow crucible and contents to cool.

5.7. Place crucible in a covered beaker containing 120 ml distilled water, 20 ml conc. H_2SO_4, and 5 ml 3 per cent H_2O_2. (The melt dissolves in a few minutes.)

5.8. Note the intensity of any yellow color (produced by titanium). When melt is dissolved, rinse, remove, and reserve crucible (without further cleaning) for use in 5.11 (4.4).

5.9. Precipitate $BaSO_4$ slowly by adding from a burette 50 ml barium chloride carrier solution (2 mg Ba^{++} per ml) while stirring the contents of the beaker vigorously. Let stand overnight.

5.10. Add about 1 ml 3 per cent H_2O_2. If the yellow color deepens, add more H_2O_2 until no further change occurs.

5.11. Continue analysis as for dissolved Ra^{226} in water, beginning with 4.3.

6. PROCEDURE FOR TOTAL RADIUM^{226} (INDIRECT) IN WATER

Total Ra^{226} in water can be determined as the sum of the dissolved Ra^{226} and the suspended Ra^{226}. See Sections 4 and 5. Such an approach involves more work than is necessary if only total Ra^{226} is required.

7. PROCEDURE FOR TOTAL RADIUM^{226} (DIRECT) IN WATER

Acidify the original sample with 2 per cent by volume of conc. hydrochloric acid for storage prior to analysis.

7.1. Thoroughly mix acidified sample before taking the aliquot. The aliquot taken is 1020 ml unless this volume contains more than 1 g of inorganic suspended matter. In the latter case, take an aliquot which will not contain more than 1 g of inorganic suspended matter.

7.2. To the aliquot add with vigorous stirring 50 ml of dilute $BaCl_2$ carrier solution (2 mg Ba^{++} per ml). A blank consisting of distilled water and 2 per cent HCl is similarly treated and started at this step.

7.3. Add slowly and with vigorous stirring conc. H_2SO_4 in the ratio of 20 ml per liter of aliquot taken. Cover and let stand at room temperature overnight.

7.4. Continue as with procedure for dissolved Ra^{226} in water: 4.3, 4.4 (weigh platinum vessel), 4.5 (omit HF addition), and 4.6 (weigh platinum vessel plus barium sulfate plus ashed inorganic suspended matter).

7.5. Calculate approximate weight of ashed inorganic suspended matter.

7.6. Follow procedure for Ra^{226} in suspended matter: 5.3 through 5.8, 5.9 (omit addition of barium chloride carrier), 5.10, and 5.11.

8. CALCULATIONS

8.1. Correction for Ra^{226} loss: The four methods described are quantitative. Ra^{226} losses are well below 1 per cent and corrections for loss are not needed.

8.2. Corrections for counting efficiency: The usual corrections for geometry, backscatter and self-absorption are not required, because the scintillation cell is calibrated directly by use of the essentially stable Ra^{226} standard.

8.3. The amounts of Ra^{226} in the sample bubbler and blank bubbler are calculated from the following formula:

$$\mu\mu c\ Ra = \frac{(R_s - R_b)}{R_c} \times \frac{1}{1-e^{-\lambda t_1}} \times \frac{1}{e^{-\lambda t_2}} \times \frac{\lambda t_3}{1-e^{-\lambda t_3}}$$

where λ = decay constant for Rn^{222}; $\lambda = 0.00755$/hr.

t_1 = time interval allowed for ingrowth of Rn^{222}, hours

t_2 = time interval between de-emanation and counting, hours

t_3 = time interval of counting, hours

R_s = observed counting rate of sample in scintillation cell, c/hr.

R_b = (previously) observed background counting rate of scintillation cell with compressed air, c/hr.

R_c = calibration constant of scintillation cell in counts per unit time per $\mu\mu c$ of radon plus decay products, c/hr.

The correction factors are obtained directly from Table 1 (19).

In calculating cell calibration constants, the same formula is used. The $\mu\mu c$ Ra^{226} is known and R_c becomes the unknown; the two terms are, therefore, interchanged in the formula.

For all practical purposes, 1 gram Ra^{226} equals 1 curie. Hence,

$$\mu\mu g\ Ra^{226}/l = \frac{\mu\mu c\ Ra^{226}\ (sample\text{-}blank) \times 1000}{ml\ sample}$$

$$\mu\mu g\ Ra^{226}/g\ ashed\ suspended\ matter = \frac{\mu\mu c\ Ra^{226}\ (sample\text{-}blank)}{wt.\ of\ ashed\ suspended\ matter}$$

9. PRECISION AND ACCURACY

Twelve (spiked and unspiked) water samples (in duplicate) ranging from distilled water to brine from the Great Salt Lake (TDS = 269,000 mg per liter) were analyzed by the method of Section 4 and the results were compared with results from fifteen de-emanations of two bubblers containing Ra^{226} equal to the spikes. The recovery of the dissolved radium from the samples averaged 100.2 per cent (range 96.8 per cent to 102.4 per cent; standard deviation of the mean was 0.31 per cent). The recovery from the standards was 100.0 per cent by definition (range 96.8 to 101.4 per cent; standard deviation of the mean was 0.28 per cent).

Comparable recovery data have been obtained by the procedure given in Section 5 for siliceous materials. Ra^{226} lost in the procedures, as determined by analyses of filtrates, averages 0.03 per cent for the procedure of Section 4 and 0.3 per cent for the procedures of Sections 5, 6, and 7 (19).

The precision and accuracy of the procedures are essentially the same and are controlled by the errors in counting the radon rather than by errors in the chemical aspects of the procedures. A part of the error is caused by the statistical errors in counting the samples, blanks, and cell backgrounds and in the calibrations of the cells. Both precision and accuracy are estimated to be $\pm$2.5 to 3.0 per cent at levels which are ten times the blank (0.04 $\mu\mu$g Ra^{226}) or higher. An occasional sample, perhaps one out of twenty, will not fall within the stated limits of precision and accuracy.

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